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(71) Applicant(s)

James Andrew McLaughlin
49 North Parade, BELFAST, BT8 2GH, United KingdomJohn McCune Anderson
16 Torgrange, Holywood, County Down, BT18 0NG,
United KingdomPaul Damian Maguire
139 Cliftonville Road, BELFAST, BT14,
United Kingdom

(72) Inventor(s)

James Andrew McLaughlin
John McCune Anderson
Paul Damian Maguire(51) INT CL⁶

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EP 0818801 A2 US 588594 A US 5652029 A
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(74) Agent and/or Address for Service

J A Kemp & Co.
14 South Square, Gray's Inn, LONDON, WC1R 5LX,
United Kingdom

(54) Abstract Title

RF plasma enhanced CVD where the substrate acts as a cathode

(57) An apparatus for coating a substrate with a diamond like coating or other vacuum depositable material comprises a chamber 11 having, or acting as, an anode, means for supporting a substrate 15 in the chamber, means for establishing a low pressure atmosphere containing a hydrocarbon-based gas in the chamber, and a radio frequency source 12 for establishing a gas plasma in the chamber, the substrate 15 acting as a cathode. The hydrocarbon-based gas may be acetylene and this may be mixed with an inert gas such as argon or a silicon based gas. The substrate may be a conductive tube or a wire which may be transported through the chamber from a supply means to a take up means. The anode may be formed by at least one wall of the chamber or is an element disposed in the chamber. When a continuous wire is used as the substrate it picks up charge to serve as the cathode by passing round guide wheels 110 which provide electrical connection to the guide wire 104.

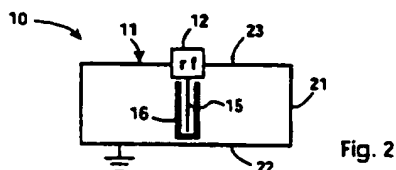


Fig. 2

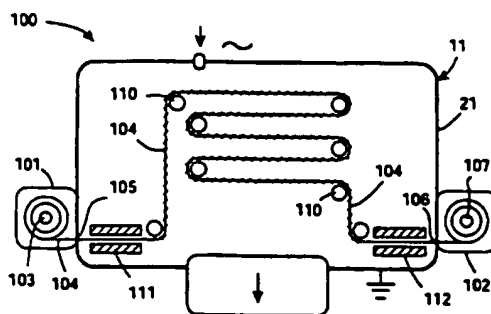


Fig. 1

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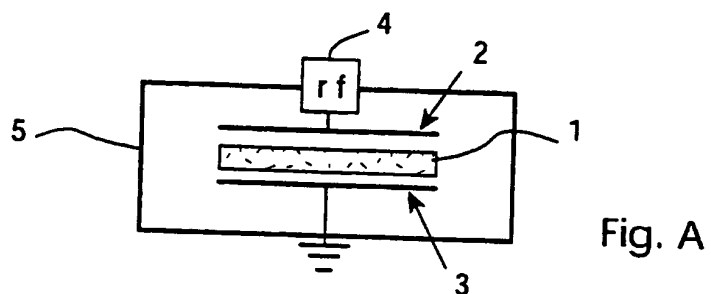


Fig. A

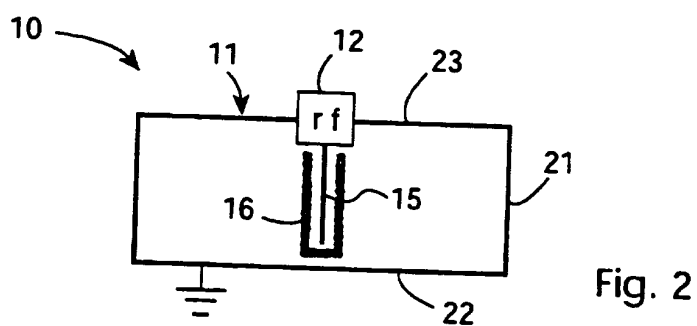


Fig. 2

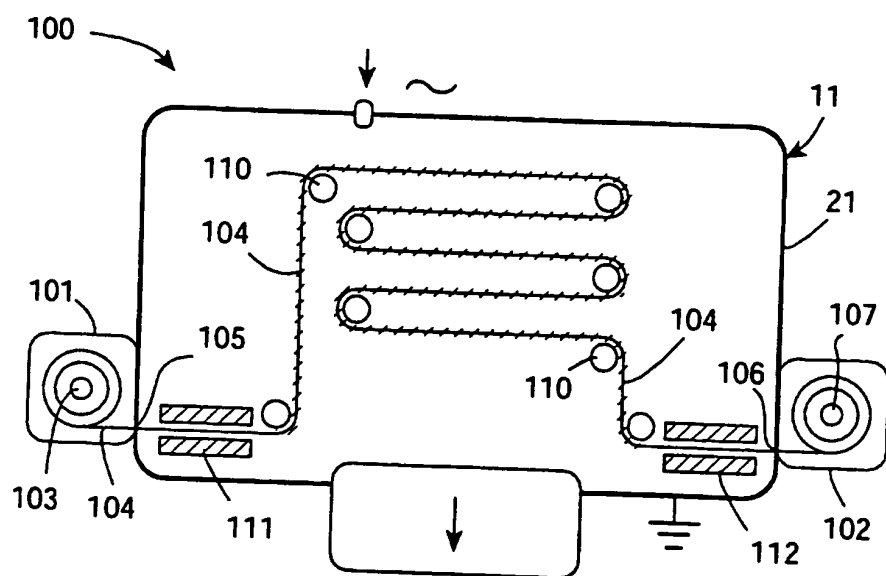


Fig. 1

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This invention relates to an apparatus and a method for coating diamond like carbon (DLC) or other vacuum depositable material onto a substrate.

- 5 DLC films or coatings is the generic term for a mixture of sp^2 and sp^3 bonded carbon and can generally be described as hard, amorphous, lubricious, impermeable, chemically inert and possessing high electrical resistivity proportions.
- 10 Presently medical device coatings such as polytetrafluoroethylene (PTFE) or Silicone overlays are applied by dip coating or electrostatic spraying methods thus forming a 200-300 μ m thick outer layer.
- 15 Traditionally these coating techniques have associated problems including poor metal to polymer adhesion and non uniformity of coating. The nature of these coating techniques leads to poor process control due to the fluid dynamics of thick films, poor yields due to
- 20 adhesion and poor uniformity and large non-environmentally friendly waste.

The most commonly used technique for coating guide wires is electrostatic spraying which gives rise to

25 non-uniform coatings and requires the need for interlayers between the substrate and coating to achieve acceptable adhesion. Additionally excessively thick coatings subsequently adds rigidity to the substrate which may be, for example, a wire or a

spring. Furthermore the process gives rise to loosely bonded aspirates which are not acceptable where the substrate is designed for internal use such as medical devices for body implantation.

5

Thus, for example, medical grade stainless steel guide wires are currently used to aid the introduction of catheters and other medical devices into the human body. The device in a coated or uncoated state must
10 exhibit good flexibility, low surface roughness, possess a high chemical resistance and conform to biocompatibility standards. The device requires surface hardness as it has to be threaded through a metal needle; high flexibility and low surface
15 coefficient of friction in order to aid the movement through channels in the body; and good biocompatibility properties due to the nature of the *in vivo* procedure.

In the prior art, and with reference to Figure A of the
20 Drawings, plasma based coating systems, such as sputtering, and normal RF plasma enhanced chemical vapour deposition chambers, employ the use of parallel plate or conical facing electrodes that only allow 'in the plane of sight' coating. Thus rotation of the
25 substrate is required. Thus in the case of, for example, sputtering, in Figure A, the substrate 1 is interposed between two plates 2, 3 in a chamber having walls 5. The plate 2 acts as a cathode; the plate 3 acts as an anode or the walls 5 act as an anode. A

source of radio frequency voltage is provided from a source 4. Apart from the need to rotate the substrate 1 relative to the plates 2,3, the coating of the substrate is uneven, non-uniform and non-conformal.

5 This is particularly the case where the surface of the substrate is, at the microscopic level, uneven.

It is an object of the present invention to provide an apparatus for applying a conformal DLC coating, or
10 other vacuum depositable material, to a substrate.

The invention, therefore, provides an apparatus for coating a substrate with a diamond like coating or other vacuum depositable material, the apparatus
15 comprising a chamber having an anode, means for supporting a substrate in the chamber, means for establishing a low pressure gaseous atmosphere in the chamber, and a radio frequency source for establishing a gas plasma in the chamber, the substrate acting as a
20 cathode.

The invention further provides a method for coating a substrate with a diamond like coating or other vacuum depositable material, the method comprising supporting
25 a substrate in a chamber having an anode, establishing a low pressure gaseous atmosphere in the chamber, and establishing a gas plasma in the chamber using a radio frequency source, the substrate acting as a cathode.

By providing an apparatus in which the substrate is the cathode and the wall or preferably walls of the chamber function as the anode, the substrate may remain static, i.e. rotation of the substrate is not required in order to uniformly coat the substrate. This is particularly advantageous where the substrate comprises, in the microscopic sense, a rough surface. Alternatively, the anode may comprise a plate inside the chamber or may comprise a tubular element in the chamber and into which element the substrate is placed. Instead of using a tubular element, a pair of oppositely disposed hemispherically shaped elements could act as an anode. As a further alternative, the chamber itself could be tubularly shaped in which the curved wall is an anode. In use, a coaxial plasma can form between the cathode and the anode electrode arrangements that are spaced typically over ranges of between 2cm and 30cm although this gap can be larger or smaller. The geometry of the anode electrode may be circular or square but in the case of a short gap of the order of a few cms it is preferred, for a conformal coating, that the anode is circular. In the case of a wide gap i.e. greater than 10cm the geometry of the anode is less important and a square/rectangular arrangement can be utilised due to the nature of electric field confinement over larger distances on small diameter substrates.

The invention will be understood in greater detail from the following description of the preferred embodiments

thereof by way of example only in which:

Figure A is a schematic view of a prior art apparatus;

Figure 1 is a schematic view of a first embodiment
5 of an apparatus according to the invention; and

Figure 2 is a schematic view of a second embodiment of an apparatus according to the invention.

Referring now to Figures 1-2 of the drawings and in
10 particular to Figure 1 thereof, there is shown a first embodiment of an apparatus 10 according to the invention which comprises a chamber 11 having walls 21, a base 22 and a top 23. Associated with the chamber is a radio frequency source 12. An opening (not shown) is
15 provided to enable a gas or gas mixture to be introduced into the chamber. Such a gas mixture is preferably Argon/acetylene or any other hydrocarbon based gas in a preferred ratio of 1:3. If desired, a silicon based gas may also be introduced in which case
20 the ratio is preferably Argon:Acetyene:Silicon based gas = 1:3:2. The working pressure of the gas or gas mixture within the chamber is preferably between about 1.06Pa - 1.33Pa (8 - 10mT). The radio frequency is typically about 13.56 MHz giving rise to a self bias DC
25 voltage of about 450V. The power density is typically about 1 to 10 W/cm².

A substrate 15 is introduced into the chamber 11. In the present embodiment the substrate is in the form of

an electrically conductive guide wire, but it could be a conductive tube. The guide wire is connected to the cathode terminal of the electrical source. At least one of the walls 21 and preferably all the walls 21 are
5 connected to the electrically anode (earthed) side of the electrical source. Thus, the wall or walls 21 can function as a anode while the substrate 15 functions as an cathode. An Example of the process condition applicable to the apparatus 10 is:

10

Gas Ratios:	Argon:1/Acetyene:3/Silicon based gas:2
Working Pressure:	1.33Pa (10mT)
Film Thickness:	0.5 μ m (Surface roughness > 10nm)
15 Film Thickness:	0.1 μ m (Surface roughness < 10nm)
Power density:	1 W/cm ²
Self DC bias:	- 450 Volts

This arrangement will allow for a conformal coating on
20 a conductive substrate having a wide range of geometrical shapes such as spring wound guide wires whereby the interstices are uniformly coated which is unlike the thick and uneven film coatings of the prior art. Where the substrate 15 is a guide wire, a uniform
25 and conformal film coating as obtained in the present invention will provide a smoother passage for the guide wire when in use. The hydrocarbon based gas is ionised within the plasma allowing a range of positively and negatively charged species to be

obtained. The positively charged ions are attracted to the cathode and cause controlled ultra thin film growth due to condensation on the substrate. The invention allows optimisation of this growth mechanism due to the particular characteristics such as high plasma densities that arise from the co-axial plasma arrangement and the high rate of surface modification occurring prior and during film deposition. Films as thick as 2 microns can be grown with high hardness and low stresses.

As will be observed, rotation of the substrate is not required in order to provide a uniform coating. Substrate heating to improve adhesion of the sample is not required and deposition takes place at room temperatures, unlike the other plasma based designs mentioned. The invention as illustrated will apply a RF voltage to the electrically conductive substrate allowing it to set a potential difference across a gap (defined by the debye length) thus allowing a co-axial plasma to form. The large DC bias (typically about 450 volts) is provided thereby allowing a high control of film deposition and thus film quality. The nature of the plasma will be unique to this configuration as it will have the ability to conformally surround the substrate. This in turn means that uniform coating of a rough surface is possible and the nature of the co-axial plasma gives rise to highly dense plasma phases. The apparatus 10 has the ability to produce

ultra-thin or thick conformal films of DLC with hardness, adhesion and low coefficient of friction values much better than those found in prior art planar electrode coating systems, electrostatic or dip coating technologies. The ability to produce ultra thin forms of DLC using the coaxial technique allows low stress coatings which will not de-laminate during elongation of the wire or device.

10 The present invention ensures that loosely bonded contamination is eliminated and wetability of the surface of the substrate 15 is improved. A plasma polymerised polymeric layer is deposited in order to promote the adhesion of the DLC layer and allow the formation of a graded interface with subsequent layers, although this is not always necessary. Because high density co-axial electrical fields surround the substrate 15, a focused field subsequently gives rise to a focusing effect on the trajectory of the incoming bombarding ions at the cathode. This will produce a deposition process that will have a higher deposition rate and more energetic ion bombardment of the substrate will occur. This will have the effect of higher hardness, higher adhesion and lower surface coefficients of friction due to the ability to former higher levels of sp^3 carbon. As a result, a high quality growth mechanism is achieved, more normally associated with high temperature processing.

An acetylene and argon gas mix at 0.266Pa [2mT] allows high adhesion ($>400\text{kg/cm}^2$) coatings to be achieved at high deposition rates ($>10\mu\text{m/hr}$) with no substrate heating. A dense plasma with high energies allows high
5 adhesion without substrate heating.

It is possible to provide a composite DLC structure throughout the film in conjunction with other elements such as Silicon, Fluorine, Chlorine. The DLC composites
10 provided by the invention allow for much improved adhesion on multiple substrates, as well as dramatically improved surface properties. Contact angles greater than 100° have been established with Si
based DLC composites and thermal stability as high as
15 500°C can be achieved allowing high temperature annealing of structures. Medical devices such as catheters, medical wires, guide wires, heart valves, vascular grafts, stimulation/sensing electrodes, biosensors and associated packaging as well as many
20 other applications, will all benefit in numerous ways by improving their surface-body fluid interfaces (see Table 1).

However it is well established that the wide range of
25 functionality required for today's medical devices requires composite approaches if biocompatibility and desired mechanical or electrical properties are to be selectively achieved. Specific surface coatings as thin as 50nm will exhibit enhanced surface properties

such as hard and low coefficient parameters.

Critical to the coatings process is the need for ultra-thin ($\leq 50\text{nm}$) highly uniform and conformal layers that
5 have high bond strengths to the underlying substrates. The invention provides a process wherein device surfaces are plasma modified by highly ionised gaseous species whereby surface energy and chemical functionality is dramatically altered allowing optimal
10 thin film coating structures to be deposited with high degrees of substrate bonding. Typically ultra-thin ($\leq 50\text{nm}$) adhesion promotion layers can also be utilised and graded into the functional coating. A wide range of materials provide this role such as SiO_2 , chromium,
15 silica and some plasma polymerised polymers. This phenomenon of grading thin film DLC by adjusting gas flows is one of the key aspects provided by the invention and most suitable to conformal PECVD co-axial coatings. The ultra thin nature of the film will
20 achieve low film stresses due to structural interface matching and bulk relaxation thus improving the coatings lifetime.

The invention outlined so far allows numerous medical
25 devices such as wire based structures to be mounted in the chamber and subsequently coated batch by batch. The main improvement on current techniques is the improved yield, reproducibility and coating quality benefits.

However, an alternative mass production technique would be to spool/reel to reel coat. Reference should now be made to Figure 2 of the Drawings. An apparatus 100
5 comprises a chamber 11 and walls 21 as described with respect to the apparatus 10. Located externally of the chamber 11 is a first housing 101 and a second housing 102. The first housing 101 contains a reel 103 of uncoated guide wire material 104. An opening 105 in
10 the chamber 11 is provided which enables the wire 104 to have access thereto from the housing 101. Similarly, on the opposite side of the chamber 11, an opening 106 is provided which enables coated guide wire to pass from the chamber 11 to the housing 102 and on a
15 take up reel 107. A suitable motor (not shown) provides drive for the take up reel 107.

At various locations inside the chamber 11, there is provided a plurality of guide wheels 110 around which
20 the guide wire 104 is threaded in serpentine fashion. Between the first guide wheel upstream of the plurality of guide wheels 110 and the opening 105, the guide wire 104 passes between a first shield 111 which prevents a plasma developing around the guide wire 104.
25 Similarly, between the last guide wheel and the opening 106, the guide wire 104 passes between a second shield 112 which prevents a plasma developing around the guide wire 104. The guide wheels 110 provide electrical connection to the guide wire 104 thereby enabling the

guide wire 104 to act as an cathode with the walls of the chamber 11 acting as the anode.

By providing openings 105, 106 which are relatively
5 small and ensuring that the housings 101, 102 are
subject to the same pressures as the chamber 11,
continuous coating of a relatively long length of wire
104 is enabled. Because of the insulating nature even
at high frequencies of thick layers of DLC at
10 intervals, the process allows for an oxygen plasma in
order to try to etch the surrounding walls. This is
necessary in order to maintain an electric field and
the hydrocarbon based plasma. The guide wire 104 moves
preferably at about 6cm.s^{-1} . An example of the process
15 conditions are as follows:

Gas Ratios: Argon:1/Acetylene:3
Working Pressure: 1.33Pa (10mT)
Film Thickness: 0.5 μm (Surface Roughness < 10nm)
20 Power Density: 1W/cm²
Self DC Bias: -450 Volts

The invention provides a diamond like carbon thin (DLC)
film coating which will provide enhanced bio-
25 functionality in the areas of barrier resistance, low
coefficient of friction properties (lubricity), bulk
and surface inertness, low stress, insulating, wear
resistance, biocompatibility, enhanced coating
adhesion, conformal coating thickness, high uniformity

of coating, increases flexibility of device, decreased electrostatics over other inert coatings and the ability to process a colour change in the coated layer.

- 5 Critical to ultrathin coatings is low stress, good stoichiometry, high uniformity and high adhesion. In order to tailor wear and lubricity properties, material parameters, such as surface crystallography and roughness, are important values to monitor and it has
- 10 been shown that there is a direct relationship to device performance. The invention has the ability to bulk and surface tailor the bio-functionality of a medical device.
- 15 The DLC films (a mixture of sp^3 and sp^2 bonded carbon), are generally hard, amorphous, lubricious, impermeable, chemically inert and with high electrical resistivity/breakdown strength. Recently in vitro studies have been carried out to investigate the
- 20 biocompatibility of diamond-like carbon (DLC) coatings. Cell viability measurements have shown no evidence of overt cytotoxicity and or abnormal cellular morphology. Examples of surface modifications properties are provided in Table 1.

Table 1.

Surface Modification: Material Property	Analysis	Functional Benefits	Typical Devices
Metallic Coating Noble Metals and Alloys	EDX, SPCS and SEM and AC Impedance	X-ray opaque, Biocidal activity of silver, and electrical electrode for stimulation and sensing	Catheter, Pacemakers, Electrodes and radio opaque markers
Ceramic and DLC	Cyclovaltometry, EDX, XPS and SEM and AC Impedance	Wear, Barrier resistance, electrical insulator, hard wear, inertness and biactive (porous ceramic)	Catheters, needles, electrodes, in-vivo, sensors guide wires, pacemakers, anti infection coatings on polymer tubing
Surface Roughness	AFM, Stylus, Optical	Decreases lubricity and higher surface energy	Catheters, needles, electrodes, in-vivo, sensors guide wires, pacemakers
Coating Thickness	AFM, Xray, Reflectometry, Elipsometry	Decrease coating stress. Less traumatic and increased flexibility	Balloons, functional stimulation electrodes, catheters with small lumen
Coefficient of Friction	Static and dynamic tests	Less insertion trauma and reported less infection	Catheters, needles, electrodes, in-vivo, sensors guide wires, pacemakers
Adhesion	Z-Axis pull tester	Improved adhesion with no delamination therefore longer product life.	All devices where coating is required
Wear	Pin on disc	Longer life	All devices where coating is required
Hardness	Nanoindention	Scratch and puncture resistance	Balloons, guide wires, needles, rotor blades etc.

Inert	Cyclovoltometry	No leaching and stable electrical potentials and electrode/tissue interfaces	On metal and polymer products where ionic leaching is a problem and implant electrodes
Barrier Coating	AC Impedance	Low corrosion	On metal and polymer products where ionic leaching, corrosion and water permeability is a problem e.g., optical sensing
BioFilm Resistant	OWLS, Bio-fouling tests	Improved biocompatibility and improved active device performance	In vivo sensors, smart catheters, stents, tracts respiratory tubing etc,

The invention is not limited by or to the specific
embodiments described which can undergo considerable
5 variation without departing from the scope of the
invention.

CLAIMS

1. An apparatus for coating a substrate with a vacuum depositable material, the apparatus comprising a
5 chamber having an anode, means for supporting a substrate in the chamber, means for establishing a low pressure gaseous atmosphere in the chamber, and a radio frequency source for establishing a gas plasma in the chamber, the substrate acting as a cathode.
10
2. An apparatus as claimed in claim 1, wherein the gaseous atmosphere contains a hydrocarbon-based gas so as to coat the substrate with diamond like carbon.
- 15 3. An apparatus as claimed in claim 2, wherein the hydrocarbon-based gas is acetylene.
4. An apparatus as claimed in claim 2 or 3, wherein the hydrocarbon-based gas is mixed with an inert gas.
20
5. An apparatus as claimed in claim 4, wherein the inert gas is argon.
6. An apparatus as claimed in claim 4, wherein the
25 inert gas is silicon based.
7. An apparatus as claimed in claim 4 or 5, wherein the hydrocarbon-based gas and the inert gas are further mixed with a silicon-based gas.

8. An apparatus as claimed in any preceding claim, wherein the anode is formed by at least one wall of the chamber.

5

9. An apparatus as claimed in any one of claims 1 to 7, wherein the anode is an element disposed in the chamber.

10 10. An apparatus as claimed in claim 8 or 9, wherein the anode is tubular, the substrate being disposed in the tubular anode.

11. An apparatus as claimed in any preceding claim,
15 wherein the working pressure of the gas or gas mixture within the chamber is between about 1.06Pa - 1.33Pa (8 - 10mT).

12. An apparatus as claimed in any preceding claim,
20 wherein the power density is typically about 1 to 10 W/cm².

13. An apparatus as claimed in any preceding claim, wherein the substrate is a wire or conductive tube.

25

14. An apparatus as claimed in claim 13 wherein the substrate is a wire, including means for transporting the wire through the chamber from a supply means to a take up means, the supply and take up means being

external to the chamber.

15. A method for coating a substrate with a diamond
like coating or other vacuum depositable material, the
5 method comprising supporting a substrate in a chamber
having an anode, establishing a low pressure gaseous
atmosphere in the chamber, and establishing a gas
plasma in the chamber using a radio frequency source,
the substrate acting as a cathode.
- 10
16. A method as claimed in claim 15, wherein the
substrate is not rotated in the chamber.
17. A method as claimed in claim 15 or 16, wherein the
15 substrate is at room temperature.



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Application No: GB 9914950.2

Claims searched: 1-17

Examiner: Pete Beddoe

Date of search: 9 September 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): C7F (FHB, FHE, FHX)
Int Cl (Ed.6): C23C (16/26, 16/50, 16/54)

Other: Online: WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0818801 A2 (BOC) see esp col5 lines 39-51 & fig 1	1,15 at least
X	US 5888594 (MINNESOTA) see esp col4 lines 49-65, col7 lines 4-15, col7 line 43 - col8 line 18 & fig 1	1,15 at least
X	US 5652029 (SEMICONDUCTOR) see esp col2 lines 7-60 & figs	1,15 at least
X	US 5464667 (MINNESOTA) see esp col5 lines 18-39 & fig 1	1,15 at least
X	WPI accession no 87-090402 & JP 62040375 A (KANEGAFUCHI) see abstract	1,15 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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